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**HIERARCHICAL CARBON FIBERS WITH ZnO
NANOWIRES FOR VOLATILE SENSING IN
COMPOSITE CURING (POSTPRINT)**

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AFRL/RXCCM**

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HIERARCHICAL CARBON FIBERS WITH ZnO NANOWIRES FOR VOLATILE SENSING IN COMPOSITE CURING

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ABSTRACT

Volatile management is critical to quality and consistent processing of polyimide composites. It remains difficult to measure and quantify volatiles evolved during curing, hampered by a dearth of small sensors and poor high temperature performance. Embedded sensors should be minimally parasitic and embedded within the composite in order to use for feedback during processing. For this work, we report on the foundational study needed to demonstrate the use of Zinc Oxide (ZnO) nanowire coated carbon fibers as a volatile sensor. ZnO nanowires are demonstrated to function as an ethanol sensor within a controlled environment. Growth of ZnO nanowires is shown, as well as the appropriate circuit to measure resistance. Results indicate that ZnO is a promising candidate and that relevant volatile concentrations can be measured.

1. INTRODUCTION

High temperature polymer resins continue to expand the operating space of continuous fiber reinforced composites. In particular, polyimide matrices offer high temperature performance with low density. Aerospace systems, principally those associated with turbine engines for propulsion, often require high operating temperatures sustained for the life of the system. Many components and systems are limited by material use temperature and composites in particular are often scoped with hot-wet performance in mind. Designers sometimes must replace a composite component with a metallic one on account of temperature limitations, increasing density from approximately 1.8 g/cc to upwards of 4.4 g/cc for a titanium replacement.

While polyimides are commercially available in large quantities and polyimide composites have been used for a number of years in aerospace systems, they are often excluded early in program development from design spaces on account of low maturity and high developmental risk, both to cost and schedule. More often than not, this is not due to a lack of test data or raw materials; but rather the high scrap rate and high cost of manufacturing. Polyimides are notorious for poor scaling, meaning that laboratory optimized curing conditions produce poor components on the factory floor. This forces many full scale manufacturing demonstration articles to be necessary, at great expense. Furthermore, the polyimide cure cycle is long (often 24-48 hours) and requires several precisely time steps to ensure volatile evacuation. Many problems in polyimide manufacture can be directly traced to volatile management. A more reliable method to sense volatile concentration would improve polyimide curing and reduce the engineering hours required to optimize manufacturing processes.

In this work, we begin to investigate and develop a novel sensor for use as an embedded volatile sensor. The embedded sensor will allow manufacturing and composites engineers to know when volatile formation is complete. One of the problems with many polyimide chemistries is that the temperature required to remove volatiles from the polymer overlaps with the temperature window that triggers the crosslinking reaction, as shown in the notional cure cycle in **Figure 1**. As higher temperatures are pursued to remove more volatiles and increase diffusion rates, crosslinking gradually begins to gel the resin and makes consolidation of voids impossible. We have laid the foundation to develop a sensor that will allow an operator or engineer to peer inside the composite and raise the temperature high enough to remove volatiles. The operator will then apply pressure when necessary for full consolidation, without simply guessing when volatiles are completely removed. Just as overheating a composite to guarantee volatile removal can trap voids and prevent consolidation; conservative heating and trapping of volatiles can also be problematic. Trapped volatiles are often only trapped under the pressure of the autoclave. After pressure is removed, these volatiles can expand and cause internal cracking and delaminations.

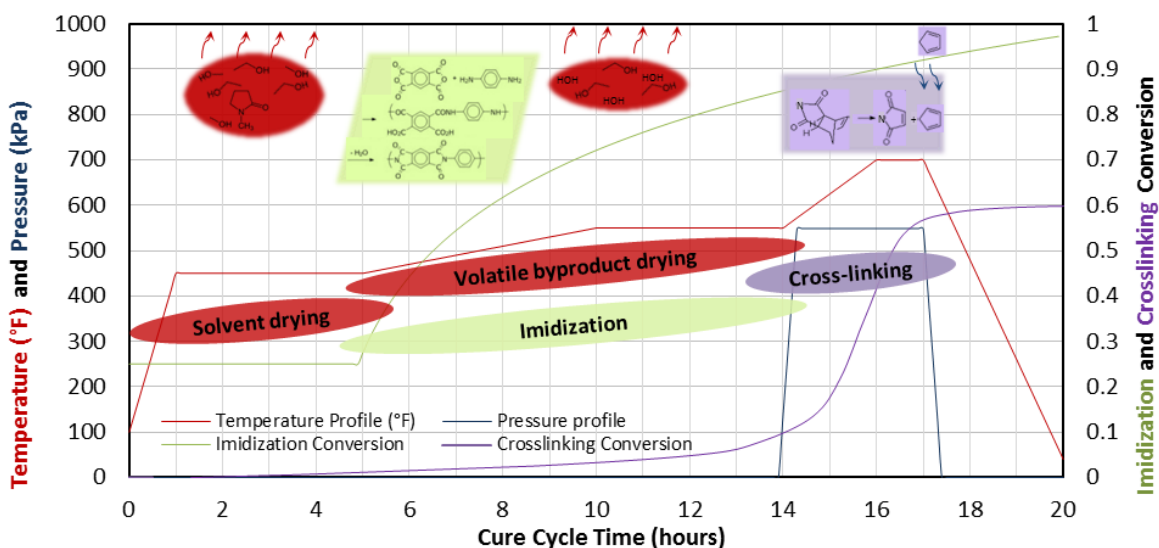


Figure 1. Representative polyimide cure cycle with overlaid regimes. The overlap volatile byproduct drying with crosslinking forces pressure application to be precisely timed to produce high quality laminates. This problem is exacerbated as thickness increases since diffusion time increases as well.

We have completed the fundamental studies required to develop a sensor that will consist of a structural carbon fiber that is coated with an array of ZnO nanowires. Zinc oxide nanowires become more conductive in the presence of ethanol – as analyte sorbs to the surface, electron density increases, dropping the resistivity by two orders of magnitude [1-5]. This resistance change can be observed in the I-V behavior, with a circuit wired up through the ZnO nanowires directly [6-10]. In order to demonstrate the proof of concept, we will show the sensitivity of ZnO nanowires to ethanol environments at various temperatures. Ethanol is a common volatile evolved and serves as a test case for this system, though we ultimately will include methanol and cyclopentadiene. Our experiments require an oven with the capability to control exposure of the ZnO nanowires to various organic molecules. Later, we will demonstrate the growth of ZnO nanowires and architecture relevant to this concept. Finally, we will conclude with an outlook for this architecture and upcoming work.

2. EXPERIMENTAL METHODS

2.1 ZnO Nanowire Synthesis

The seeding and growth of ZnO nanowire procedures are at a high risk for contamination and will prove unsuccessful if contaminants are present within the solution even in small quantities. Therefore, Tin doped Indium Oxide (ITO) coated glass slides and all other utensils were subjected to a thorough cleaning procedure. The materials were rinsed with Ultra-Pure Water (UPW), Acetone, and then Ethanol (EtOH). The order of these three rinsing agents was found to be important to ensure a successful seeding and growth attempt. The seeding solution was a 0.0125 M solution of Zinc Acetate dihydrate ($\text{ZnAc}_2 \cdot \text{H}_2\text{O}$) in EtOH. Preparation of the seeding solution started with making a 0.02M solution of Sodium Hydroxide (NaOH). Approximately 75mL of the 0.02M NaOH solution were added to a 100mL volumetric flask. Enough $\text{ZnAc}_2 \cdot \text{H}_2\text{O}$ was added to make 100mL of a 0.0125M solution. For the solution used in this experiment 0.274g of $\text{ZnAc}_2 \cdot \text{H}_2\text{O}$ was the proper stoichiometric amount. The flask was manually agitated until the zinc compound was fully dissolved within the EtOH, resulting in an optically transparent and colorless solution. The volumetric flask was then capped and mixed using a vortex mixer for 2 min. Once a uniform solution was achieved the remainder of the 0.02M NaOH solution was added to the volumetric flask filling to the 100mL fiduciary mark.

The seeding solution was then pipetted onto the conductive side of the ITO coated glass slides. After 10 seconds elapsed, the slides were rinsed with EtOH. Following the EtOH rinsing, slides were blown dry via Nitrogen (N_2) air hose. This process was replicated 4 times, resulting in 5 applications of seeds on each slide. The seeded slides were placed in an oven for 20 minutes at 350°C. After cooling, slides were placed in plastic sample bags for safekeeping.

A thorough cleaning procedure was again employed prior to the ZnO nanowire growth reaction, all materials were rinsed with Acetone, EtOH, and then UPW. To produce the growth solution, 1.49g of Zinc Nitrate Hexahydrate ($\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$) and 0.70g of Hexamethylenetetramine ($\text{C}_6\text{H}_{12}\text{N}_4$) were added to the Erlenmeyer flask. A measured quantity of 200mL of UPW was added. The solution was manually agitated by way of swirling until the solutes were fully dissolved resulting in an optically transparent solution.

A silicone oil heating bath was heated to the growth solution temperature of 90°C. A mercury thermometer was placed into the Erlenmeyer flask to monitor the growth solution temperature. Once the growth solution temperature reached 90°C, the slide was placed into the Erlenmeyer flask. The slide was placed at an approximate 45° angle leaning against the side of the Erlenmeyer flask with the seeded side facing downwards. This ensured nanowire growth was minimally disturbed by the settling of other precipitates formed within the growth solution. After 5 hours, the slides were carefully removed and rinsed with EtOH. Post rinsing, the slides were placed in an oven at 120°C for approximately 30 minutes.

2.2 ZnO Nanowire Analysis

The ZnO nanowires were first analyzed in a FEI Quanta scanning electron microscope (SEM) at 5 kV. The high resolution SEM analysis was performed with a FEI Sirion SEM at 5 kV. SEM

analysis was performed at the same magnification between various samples to provide consistent measurements of the ZnO nanowires.

2.3 ZnO Nanowire ITO Glass Slide Sensor Fabrication and Testing

After ZnO nanowires were grown on ITO coated glass microscope slides, the underlying ITO electrode was connected to the bottom of the ZnO, while the top electrode was sputtered Au/Pd deposited through a benchtop DC sputtering system. This allowed the precise patterning of the electrodes to cover a specific surface area and location along the material with a thin line of sight film. The film was then connected to a circuit with a silver epoxy ink through a tooth pick dipping. Each ZnO-nanowire on ITO Glass side sensor assembly was placed on a glass slide sample stage patterned with two voltage electrodes connected on both sides of ITO slide and two current electrodes with a 2.54 cm gap. A electrical voltage was supplied between the electrodes using a Keithley 2410 precision SourceMeter, while the current change across the fiber was measured using a LabView data acquisition system that interfaced directly with the SourceMeter control software. The resistance of the ZnO nanowires was measured along the length of the nanowire in this configuration (see **Figure 2**), with organic molecules adsorbing to the sides of the nanowires. This allowed maximum surface area (nanowire array compared to porous solid) for adsorption. Typical morphology of the nanowires is shown in **Figure 2**.

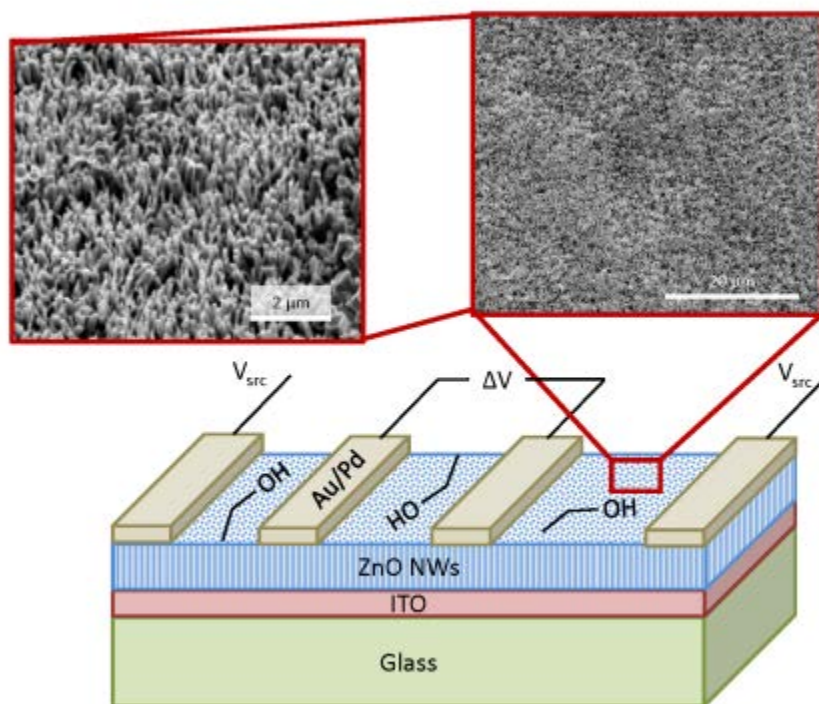


Figure 2. Schematic of electrode configuration and nanowire placement. Scanning electron microscope images show dense, naturally aligned ZnO nanowires of uniform size, consistent with previous reports.

2.4 ZnO Nanowire on Carbon Fiber Sensor Fabrication and Testing

Additionally, we have grown ZnO nanowires on carbon fiber utilizing the same chemical method, as previously described in Section 2.1. In order to ensure even coating and successful nanowire growth, the reaction must be carried out on either single carbon fibers or small tow containing relatively few carbon fibers. Carbon fiber sensors were constructed by first cutting the carbon fibers (2.54 cm long) and growing ZnO nanowires on them. The coated fibers were then dipped with Silver Epoxy on each side to form electrodes for contact with the testing circuit. Each ZnO-nanowire on carbon fiber sensor assembly was placed on a glass slide sample stage patterned with electrodes with a 2.54 cm gap. A electrical voltage was supplied between the electrodes using a Keithley 2410 precision SourceMeter, while the current change across the fiber was measured using a LabView data acquisition system that interfaced directly with the SourceMeter control software.

3. RESULTS

3.1 The Growth of ZnO Nanowire

The growth of ZnO nanowires on ITO coated glass has been extensively reported elsewhere and our results are fairly consistent with previous reports [11-15]. Nanowires are approximately 100 nm in diameter and 1 micron long, which equates to a typical aspect ratio of 10. The nanowires were deposited through a solution based two step growth method. The first step is seeding the growth, then placing the sample into the growth solution. ZnO gradually precipitates out of solution onto the seeds, which then grow competitively into nanowires. The ZnO crystals are wurtzite in structure with polar and non-polar faces. The polar faces pull ions out of solution faster with a lower energy barrier, leading to higher growth rates on these faces than alternative non-polar surfaces. The ZnO nanowires thus grow in a constant aspect ratio unless surfactants or adsorbents are used to reduce the ability of ions to add to the crystal faces. In this growth, we did not utilize surfactants to increase the aspect ratio but are investigating this for future experiments.

3.2 Environmental Exposure and Verification

A temperature controlled environment has been designed and fabricated to control ethanol vapor concentration and test sensors at elevated temperature. A Yamato ADP-31 vacuum oven was outfitted with ports for gas flow and control wires for sending and receiving the sensing signal. Ethanol vapor concentration was controlled with a vapor mass control scheme where nitrogen gas was bubbled through 100% ethanol solution, and mixed with a metered stream of nitrogen. The two mass flow controllers (Omega FVL series) are shown in **Figure 3**, along with the ethanol bubbler. As nitrogen was bubbled through the ethanol solution, we assume the vapor became saturated with vapor pressure (or moles) of ethanol so the flow control system was used to dilute the pure ethanol stream with nitrogen flow. **Figure 3** shows the vacuum oven modification set-up for this sensor testing experiment. A pressure transducer was installed in-line with the ethanol vapor line before it mixes with the nitrogen line. This line gives absolute pressure over the ethanol bath, and allows calculation of the molar concentration of ethanol stream before mixing.

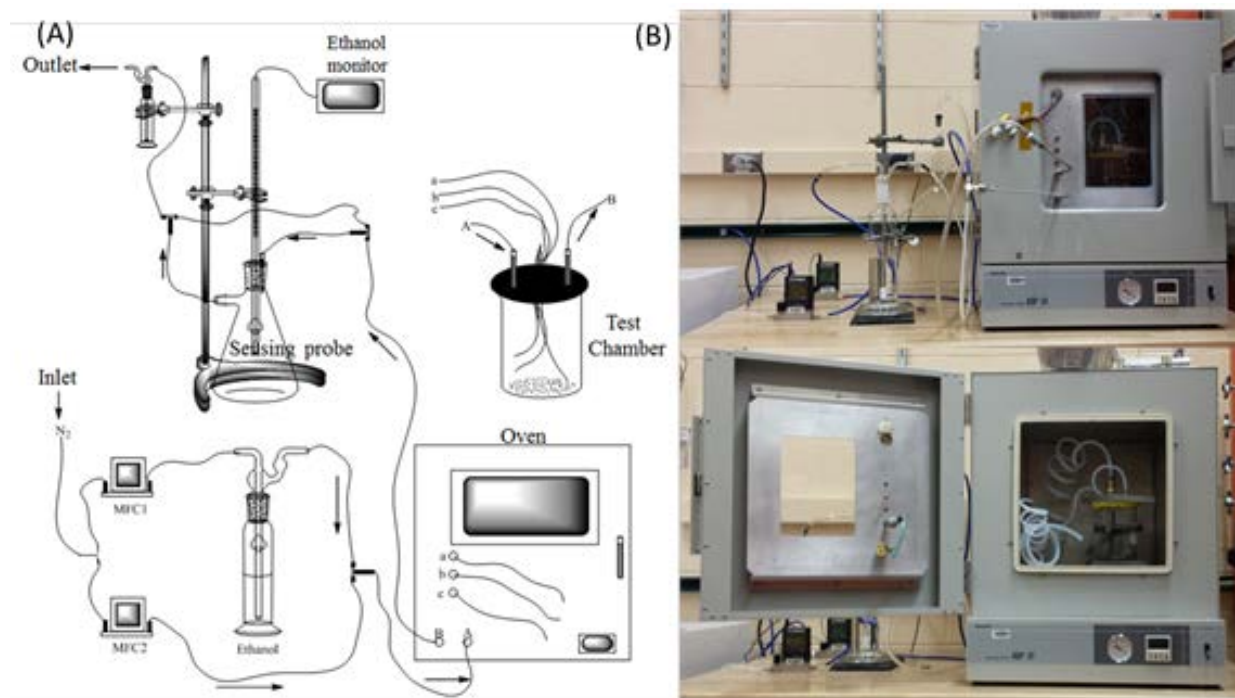


Figure 3. A) Schematic of environmentally controlled oven that shows nitrogen line splitting. One nitrogen line bubbles through pure ethanol while another bypasses and serves to dilute the incoming vapor. The two streams mix to provide a controlled concentration of ethanol vapors. After the vapors circulate through the closed chamber inside the oven, the ethanol concentration flowing out is measured with an ethanol sensor to verify system performance. B) Optical photographs of the setup with the oven open and closed.

3.3 Initial Ethanol Detection of ZnO Nanowire on Carbon Fibers

An initial study has been performed to observe the resistance changes of ZnO nanowire coated carbon fiber by using the experiment set up shown in **Figure 3**. Two test conditions were used: Nitrogen only and 99% Nitrogen with 1% ethanol. The sample, straight carbon fiber coated with ZnO nanowire, was loaded into the chamber, and the resistance measured at room temperature. The test results are shown in **Figure 4**. It is seen that the current–voltage (I–V) curves of the ZnO nanowires on carbon fiber sensor under nitrogen and 1% ethanol-nitrogen mixed gas at room temperature are both approximately linear. The electrical resistance ($1.728 \times 10^4 \Omega$) when exposed to 1% ethanol-nitrogen gas mixture is smaller than that of the ethanol free test ($1.782 \times 10^4 \Omega$) as seen in the calculations listed in **Table 1**.

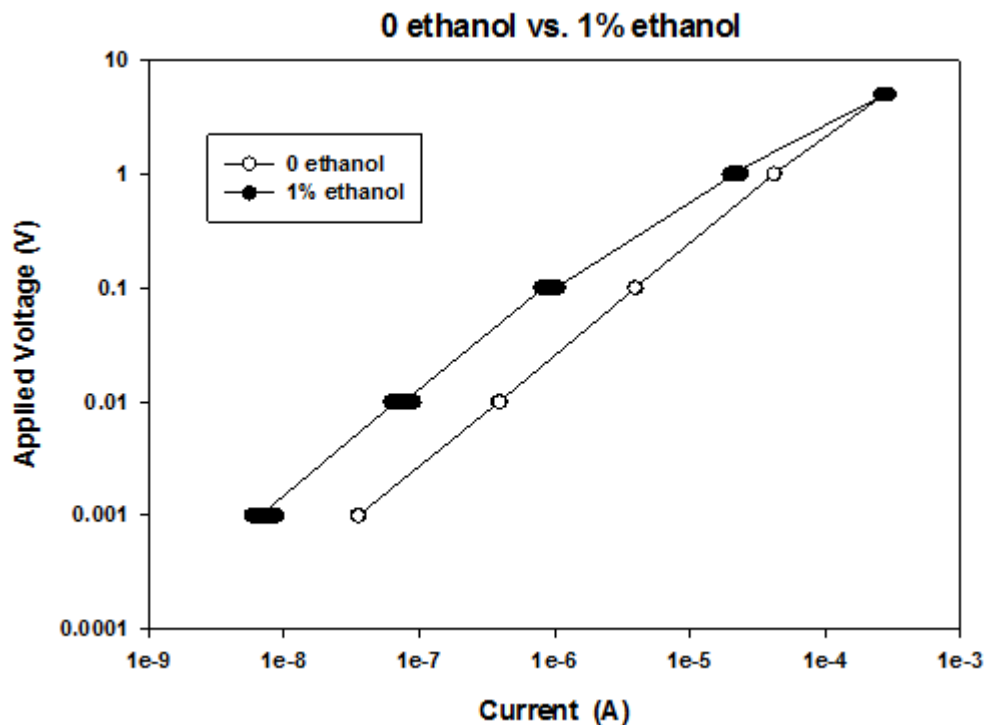


Figure 4. I-V characteristics of ZnO nanowire coated carbon fiber sensor exposed to 1% ethanol vapor and 0% ethanol (N_2) vapor at room temperature. The shift in the lines indicates that the ethanol changes the conductivity of the ZnO nanowires.

Table 1. ZnO-NW on carbon fiber exposed to 0% ethanol (N_2) and 1% ethanol at room temperature

Sample	Resistance (Ω)	Resistivity (Ω cm)	Conductivity (S/cm)
ZnO-NW on CF N_2	1.782×10^4	4.526×10^4	2.209×10^{-5}
ZnO-NW on CF 1% Ethanol	1.728×10^4	4.389×10^4	2.278×10^{-5}

3.4 Initial Ethanol Detection of ZnO Nanowire on ITO Glass Slides

Electrical resistance measurements were taken using a standard four-point monitoring system. Potential was introduced to the sensor via the outer electrodes while the corresponding current was measured via the inner electrodes. Relatively low levels of voltage were passed through the system. The maximum voltage that produced useable results was on the order of 5Volts. It was observed that ZnO nanowires have sensitivity when exposed to EtOH even at low levels of voltage. An optimum response was detected at levels on the order of 0.0001Volts.

Figure 5 shows current–voltage (I–V) characteristics of the ZnO nanowires on ITO glass slides sensor under ethanol vapor at different temperatures using 1% ethanol concentration. The curves are linear at room temperature, indicating that the sputter coated Au/Pd and silver paint electrodes form Ohmic contact with the ZnO nanowires, as found in other studies [3,4]. From **Figure 5**, we also see the effect of the temperature on the electrical resistance of the ZnO nanowires on ITO glass slides sensor at 1% ethanol concentration. We observe that as the

temperature increases from room temperature to 200°C, the resistance of the sensor decreases from $2.695 \times 10^2 \Omega$ to $5.208 \times 10^1 \Omega$ in 1% ethanol (see **Table 2**). Thus, when the ITO glass slide nanowire sample is exposed to ethanol, the gas acting as a reducing agent donates electrons to ZnO nanowires, which increases the carrier concentration of ZnO nanowires, and thus, the resistance decreases.

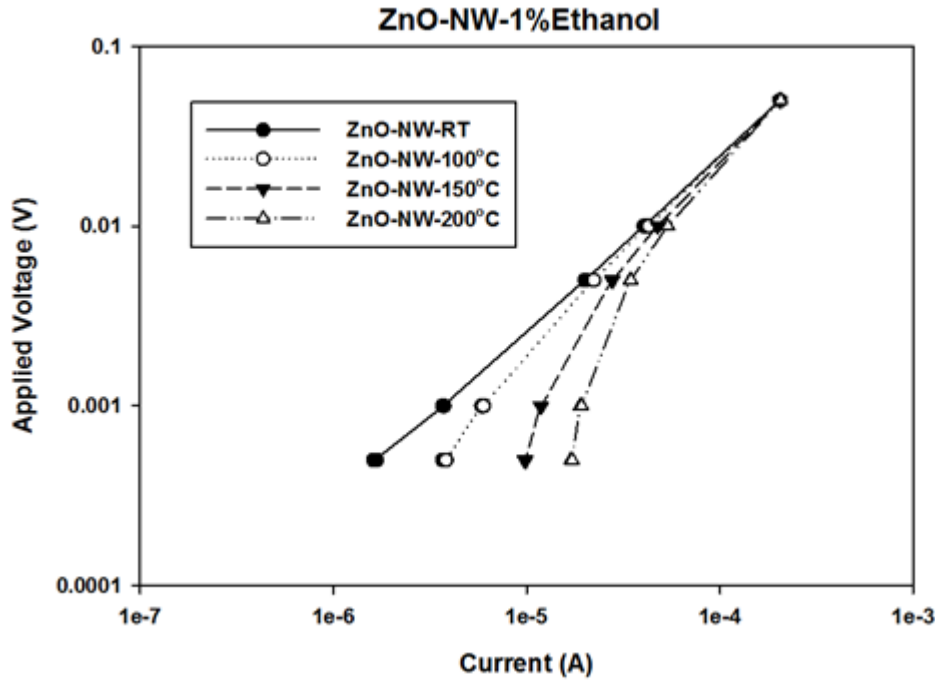


Figure 5. I-V characteristics of the ZnO nanowire coated ITO glass slides sensor exposed to 1% ethanol vapor at different temperatures.

Table 2. ZnO-NW on ITO glass slide sensor exposed to 1% ethanol vapor at different temperatures and 0.001 Volts

Temperature (°C)	Resistance (R, Ω)	Resistivity (ρ , Ω cm)	Conductivity (σ , S/cm)
RT	2.695×10^2	6.854×10^2	1.459×10^{-3}
100	1.686×10^2	4.282×10^2	2.335×10^{-3}
150	8.403×10^1	2.134×10^2	4.686×10^{-3}
200	5.208×10^1	1.323×10^2	7.559×10^{-3}

The sensitivity (S), of the sensor can be defined as $S = R_{\text{EtOH}}/R_{\text{N}_2}$, where R_{EtOH} is the electrical resistance of the sensor in ethanol-nitrogen mixed gas, and R_{N_2} is its resistance in nitrogen [1]. The sensitivity versus temperature at 1% ethanol is shown in **Figure 6**. It is seen that the sensitivity increases as the temperature increases from room temperature to 100°C; and with further temperature increase, the sensitivity decreases. The sensitivity increases sharply between room temperature and 100°C, this is mainly because of the competition between the mobility of ethanol molecules and the absorption of ethanol. Within this temperature range, the absorption of

ethanol plays a significant role. Beyond 100°C, the mobility of ethanol molecules becomes greater as the temperature is increased leading to a lowering of the sensitivity.

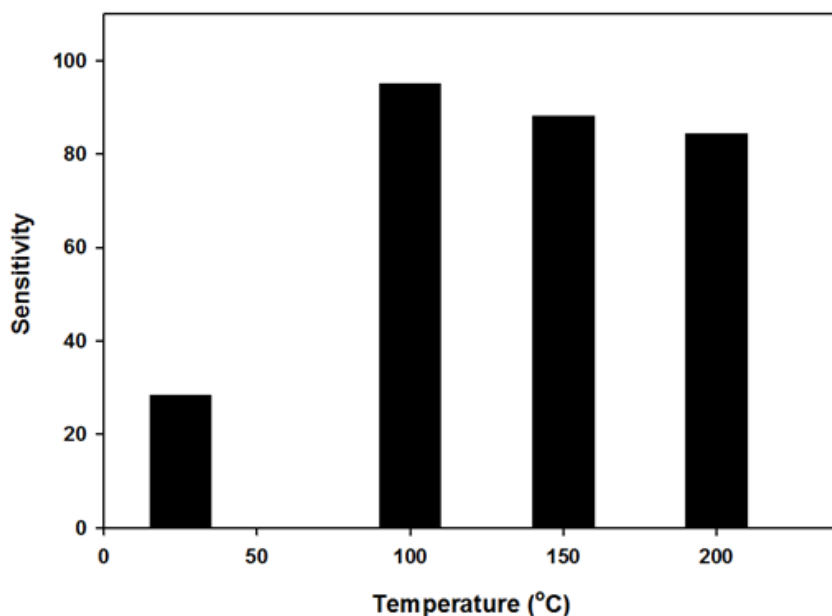


Figure 6. Sensitivity vs. working temperature at 1% ethanol concentration

3.5 Future Architecture

The architecture desired for this research is a hierarchical carbon fiber coated with nanowires grown in radially aligned direction, as shown in **Figure 7**. This architecture lends itself to the sensor, while minimizing the presence of defects in the composite. Hierarchical fibers are known to either increase or maintain interfacial properties, owing to the increased interlocking and increased surface area. Further work will utilize this fiber for volatile sensing.

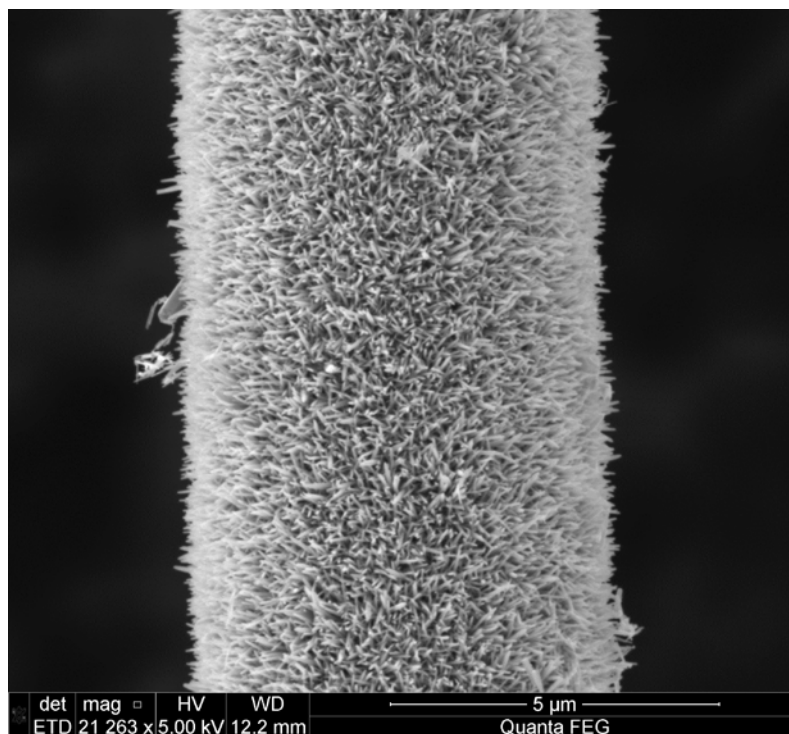


Figure 7. Radially grown ZnO nanowires coated carbon fiber

4. CONCLUSIONS

A novel volatile sensing architecture has been proposed to assist in the processing of high temperature polyimides. Growth methods for ZnO nanowires on ITO coated glass and carbon fibers have been demonstrated. ZnO nanowires show sensitivity to ethanol concentration at room and higher temperatures. Initial experiments demonstrate feasibility of implementing the sensor methodology inside a composite material in order to improve process control and inform volatile management strategies.

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